

Title: Pillared Clays as Superior Catalysts for Selective Catalytic Reduction of NO
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Grant NO. DE-FG22-96PC96206

Removal of NO_x ($\text{NO} + \text{NO}_2$) from exhaust gases is a challenging problem. V_2O_5 -based catalysts are commercial catalysts for selective catalytic reduction (SCR) with NH_3 for stationary sources. However, for diesel and lean-burn gasoline engines in vehicles as well as for stationary sources, hydrocarbons would be the preferred reducing agents rather than NH_3 because of practical problems associated with the use of NH_3 (i.e., handling and slippage through the reactor). The noble-metal three-way catalysts are not effective under these conditions. The first catalyst found to be active for selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen was copper exchanged ZSM-5 and other zeolites, reported in 1990 by Iwamoto in Japan and Held et al. in Germany. Although Cu-ZSM-5 is very active and the most intensively studied catalyst, it suffers from severe deactivation in engine tests, mainly due to H_2O and SO_2 .

In the last two annual reports, we reported Cu-exchanged pillared clays as superior SCR catalysts. During the past year we explored the possibilities with MCM-41, a new class of molecular sieves. Because it has high thermal stability, high BET surface areas and large pore volumes, MCM-41 has already attracted considerable interests in recent years. It has been studied as catalysts, support and sorbents. In this work, we investigated the activity of Cu-exchanged Al-MCM-41, platinum doped MCM-41 and Rh-exchanged Al-MCM-41 catalysts in SCR of NO with hydrocarbons in the presence of excess oxygen. Some results are summarized in Table 1.

The SCR of NO by ethylene was first investigated on copper ion and/or cerium ion-exchanged Al-MCM-41 in the presence of excess oxygen. Ce-Al-MCM-41 showed little activity, but Cu-Al-MCM-41 and cerium promoted Cu-Al-MCM-41 (i.e., Ce-Cu-Al-MCM-41) were found to be active in this reaction. A high NO conversion to N_2 , almost the same as Cu-ZSM-5, was obtained on the Ce-Cu-Al-MCM-41 catalyst. Temperature program reduction results indicated that only isolated Cu^{2+} and Cu^+ ions were detected in the Cu^{2+} -exchanged Al-MCM-41 samples, which may play an important role in the selective catalytic reduction of NO to N_2 . After some cerium ions were introduced into Cu-Al-MCM-41, Cu^{2+} in the molecular sieve became more easily reducible by H_2 . This may be related to the increase of catalytic activity of NO_x reduction by ethylene.

0.5-5 wt% Pt/MCM-41 catalysts were studied for SCR of NO with CH_4 , C_2H_4 , C_3H_6 and C_3H_8 in the presence of excess oxygen. The catalysts had high BET surface areas ($> 900 \text{ m}^2/\text{g}$) and large pore volumes ($> 1.00 \text{ cm}^3/\text{g}$). Platinum metal particles were detected in these catalysts at room temperature by XRD. A high activity for NO reduction was obtained when C_2H_4 or C_3H_6 was used as the reductant and the maximum NO reduction rate reached $4.3 \text{ mmol/g}\cdot\text{h}$ under the conditions of 1000 ppm NO, 1000 ppm C_3H_6 , 2% of O_2 and He as balance; but no or little activity was found

when CH₄ or C₃H₈ was used. This difference was related to the different nature of these hydrocarbons. The Pt/MCM-41 catalyst showed a good stability. H₂O and SO₂ did not cause deactivation of the catalyst. MCM-41 provided the highest specific NO reduction rates for Pt as compared with all other supports reported in the literature, i.e., Al₂O₃, SiO₂ and ZSM-5.

Rh exchanged Al-MCM-41 was studied for SCR of NO by C₃H₆ in the presence of excess oxygen. It showed a high activity in converting NO to N₂ and N₂O at low temperatures. *In situ* FT-IR studies indicated that Rh-NO⁺ species (1910-1898 cm⁻¹) was formed on the Rh-Al-MCM-41 catalyst in flowing NO/He, NO+O₂/He and NO+C₃H₆+O₂/He at 100-350 °C. This species was quite active in reacting with propylene and/or propylene adspecies (e.g., π -C₃H₅, polyene, etc.) at 250 °C in the presence/absence of oxygen, leading to the formation of the isocyanate species (Rh-NCO, at 2174 cm⁻¹), CO and CO₂. Rh-NCO was also detected under reaction conditions. A possible reaction pathway for reduction of NO by C₃H₆ was proposed. In the SCR reaction, Rh-NO⁺ and propylene adspecies react to generate the Rh-NCO species, then Rh-NCO reacts with O₂, NO and NO₂ to produce N₂, N₂O and CO₂. Rh-NO⁺ and Rh-NCO species are two main intermediates for the SCR reaction on Rh-Al-MCM-41 catalyst.

Table 1 Catalytic performance of MCM-41 catalysts for selective catalytic reduction of NO with hydrocarbons at different temperatures

Catalyst	Temp. (°C)	NO Conv. (%)	NO Conv. to N ₂ (%)	NO Conv. to N ₂ O (%)	C _x H _y Conv. (%)
Cu-Al-MCM-41	400	14.0	14.0	0	44.5
	450	23.0	23.0	0	83.0
	500	22.0	22.0	0	99.5
	550	9.0	9.0	0	100
	600	4.0	4.0	0	100
Ce-Cu-Al-MCM-41	400	26.2	26.2	0	29.6
	450	32.0	32.0	0	71.3
	500	36.0	36.0	0	90.4
	550	38.0	38.0	0	100
	600	28.0	28.0	0	100
1.0% Pt/MCM-41	200	4.0	2.2	1.8	4.0
	225	8.0	4.4	3.6	10.2
	250	61.0	16.9	44.1	100
	275	49.0	15.2	33.8	100
	300	36.0	11.6	24.4	100
5.0% Pt/MCM-41	200	7.0	1.3	5.7	3.3
	225	20.0	6.7	13.3	13.2
	250	63.6	15.4	48.2	100
	275	61.0	13.2	47.8	100
	300	47.0	10.6	36.4	100
Rh-Al-MCM-41	250	34.0	20.5	13.5	43.1
	275	68.2	47.1	21.1	100
	300	44.9	29.6	15.3	100
	325	33.5	21.8	11.7	100
	350	23.5	15.7	7.8	100

Conditions: 0.5 g of sample for Cu-Al-MCM-41 and Ce-Cu-Al-MCM-41, 0.1 g for Pt and Rh catalysts, [NO] = 1000 ppm, [C₂H₄] (for Cu) or [C₃H₆] (for Pt, Rh) = 1000 ppm, [O₂] = 2%, He = balance, total flow rate = 250 ml/min.

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Students Receiving Support:

M. Sirilumpen, N. Chen, N. Tharapiwattananon, R.Q. Long (Postdoctoral).